Review of Biogenic Volatile Organic Compounds and Their Products

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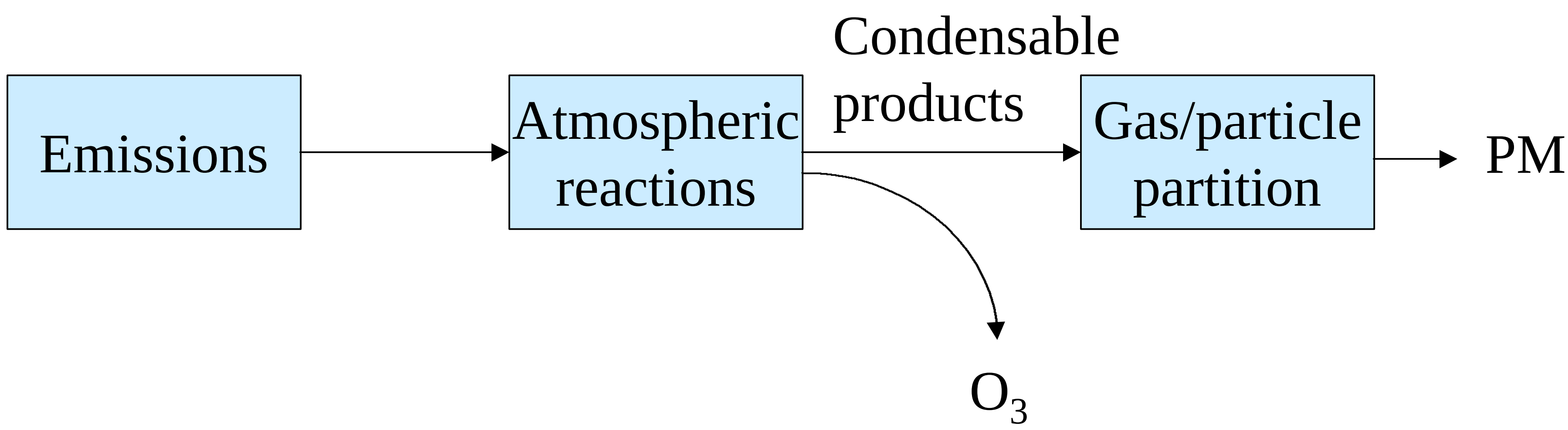
Introduction

Biogenic compounds are precursors to ozone (O_3) and particulate matter (PM)



Biogenic Volatile Organic Compounds

	Emission % in North America
• Isoprene	31%
• Methylbutenol (MBO)	5%
• Monoterpenes + sesquiterpenes	22%
• Reactive oxygenates	16%
• Less reactive oxygenates	26%

Isoprene

- Sampling, analytical, eddy covariance flux methods are well-developed

Emission Characteristics

- Dominant VOC
- From deciduous species and spruce
- During day-light hours only
- Depends on leaf temperature and PAR

Isoprene Data Needs

- Vegetation types other than oaks, poplars, aspen, and spruce
- Effects of temperature history and season
- Landcover data

Monoterpenes

- Predominant compounds: α-, β-pinene, limonene, and Δ^3-carene

Emission Characteristics

- From conifers and some deciduous species
- Depends on temperature
  - Some Mediterranean oaks emit terpenes with isoprene-like light, temperature dependence

Monoterpene Data Needs

- Emission capacities of individual monoterpene compounds
- Characterization of emission response to
  - rainfall / humidity
  - herbivory
- Canopy-scale measurements
- Comparison of measurements and inventory models

Sesquiterpenes

- Semivolatile, low emission capacities
- May contribute up to 16% of total BVOC landscape-scale flux

<u>Data Needs</u>

- Identification of individual sesquiterpenes and their emission capacities
- Canopy-scale measurements
- Regional emissions estimates

Oxygenated VOC

- Methylbutenol, emitted via the light-dependent chloroplast mechanism
- Other oxygenates emitted by defense mechanisms or cut and drying vegetation
- Regional emissions difficult to quantify due to intermittent emissions
- No canopy-scale information
- No evaluation at landscape scale

Biogenic Emissions Modeling

$$F = eDgdr$$

ε = area-average emission capacity

D = foliar density

γ = activity factor for light, temperature, leaf age

δ = activity factor for other factors

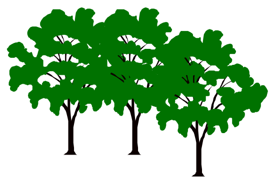
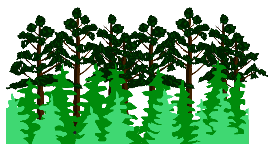
ρ = canopy escape efficiency

Canopy Modeling

- Microclimate within a forest canopy as a function of height
  - temperature (heat flux)
  - PAR

Measurements and Modeling (Isoprene)

- Measurement scale-up studies

  - – 40% difference between leaf and canopy scales
- Reconciliation of measurements with models
  - – 30% difference between flux measurement and model for site specific applications
  - – factor of 1.2 to 2 using inverse modeling of ambient concentrations

Chemical Functionality

- Saturated aliphatics
  - Alkanes, alcohols, aldehydes, ketones, acids, esters, ethers
- Aromatics
- Unsaturated Aliphatics
  - Alkenes, dienes, terpenes (1 to 3 C=C), sesquiterpenes (1 to 3 C=C)
- Unsaturated Oxygenates
  - alcohols, esters, aldehydes, ketones

Kinetics of Saturated Aliphatics and Aromatics

- Saturated aliphatics react only with OH
- Aromatics react mainly with OH, NO_3 may be a minor pathway
- Missing kinetic data for hexanal, camphor, cineole, and p-cymene can be estimated by structure-reactivity relationships
- Acetone has the maximum $\tau_{1/2}^{(1)}$ = 36 days
- Hexanal has the minimum $\tau_{1/2}^{(1)}$ = 6 hours

(1) OH = 10^6 molec/cm^3

Kinetics of Unsaturated Compounds

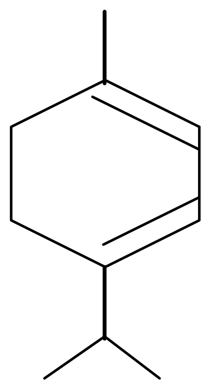
Unsaturated VOC react with OH, O_3, and NO_3

	$\tau_{1/2,OH}^{(1)}$ (hours)	$\tau_{1/2, O3}^{(2)}$ (hours)
alkenes	3.0 - 23	1.3 - 160
isoprene	1.9	20
terpenes	0.53 - 3.6	0.01 - 280
sesquiterpenes	0.65 - 4.1	0.02 - >500
oxygenates	1.2 - 6.6	0.60 - 130

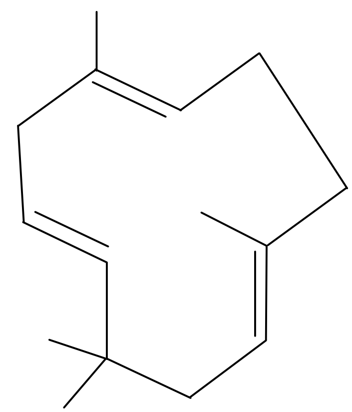
(1) OH = 10^6 molec/cm^3; (2) O_3 = 30 ppb

Highly Reactive Compounds

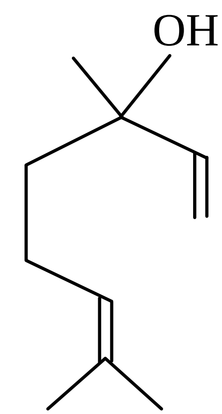
α-terpinene



α-humulene



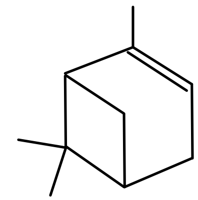
Linalool



Reaction with O_3 may be the dominant removal process for the more reactive BVOC

First-Generation Products

- Example: OH + α-pinene



  - Pinonaldehyde, acetone, formaldehyde
  - Organic nitrates, hydroxy nitrates, dihydroxy nitrates, dihydroxycarbonyls
- For O_3 and OH reactions
  - Detailed information for alkenes, α-, and β-pinene, and unsaturated alcohols
  - Limited or no information for >20 BVOC
- Less information on NO_3 reaction

SOA Formation

- 14 BVOC known to form SOA
  - 10 terpenes (α-pinene most studied)
  - 2 sesquiterpenes
  - 2 unsaturated alcohols
- Isoprene does not form SOA
- SOA composition studied for 5 BVOC (reactions with O_3 and OH only): α-, β-pinene, d-limonene, terpinolene, Δ^3-carene

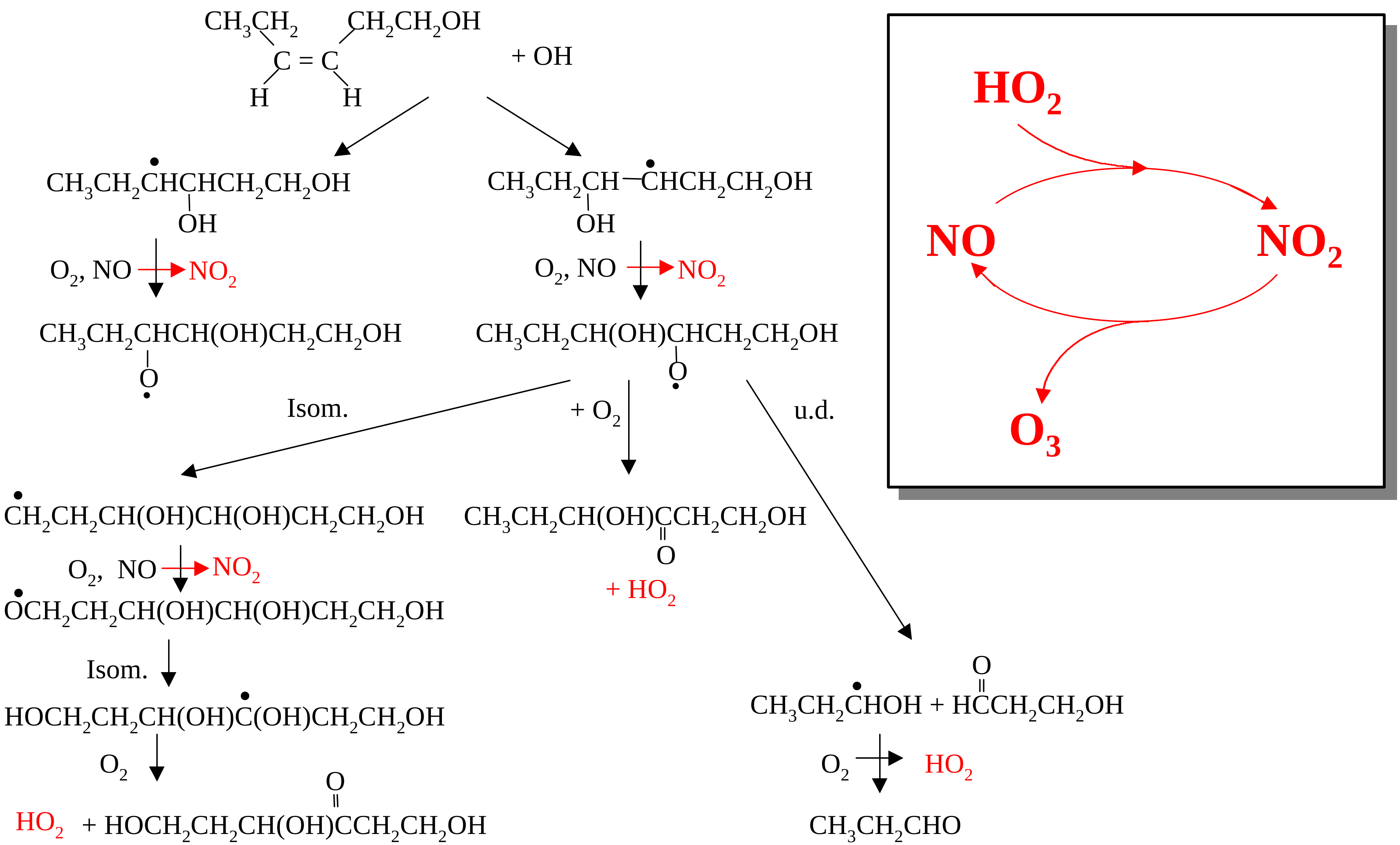
Reactions of First-Generation Products

- Kinetic data for first-generation products are limited
  - Aldehydes removed rapidly by OH reaction
  - Unsaturated carbonyls react with O_3
- Product studies conducted for only 6 first-generation compounds
  - Very limited information on second-generation products

Detailed BVOC Mechanisms

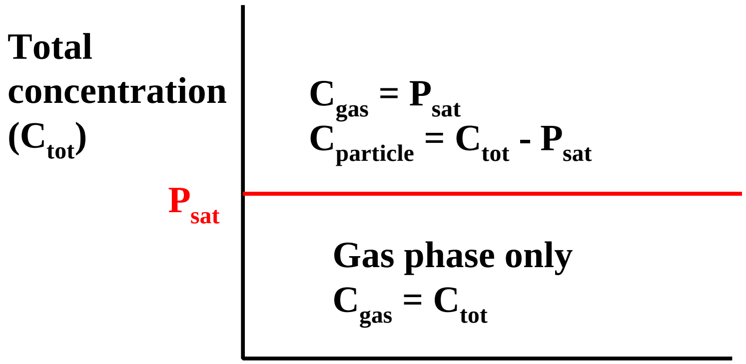
- With the exception of isoprene and α-pinene, detailed mechanisms cannot be constructed for BVOC

O_3 Formation from BVOC

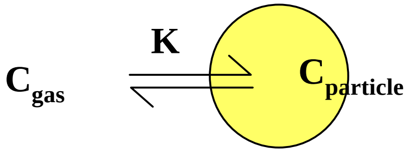


Organic Aerosol Partition Theories

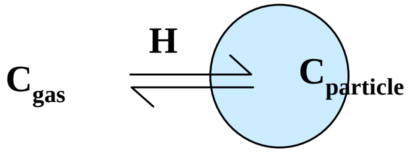
- Saturation
  - Fixed yield approach



- Absorption into an organic phase



- Aqueous dissolution



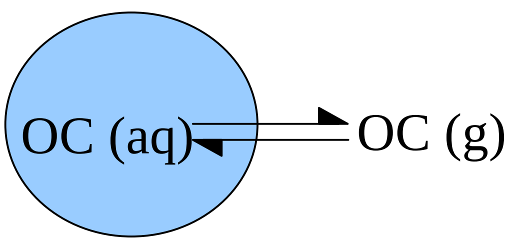
Existing SOA Modules

Models-3, DAQM2	1. Fixed yield 5 products 2. Absorption 6 products
SAQM-AERO	Fixed yield
UAM-AERO	Absorption (Raoult's law) 6 products
Models-3/EPRI	Absorption (Griffin/Odum) 34 products

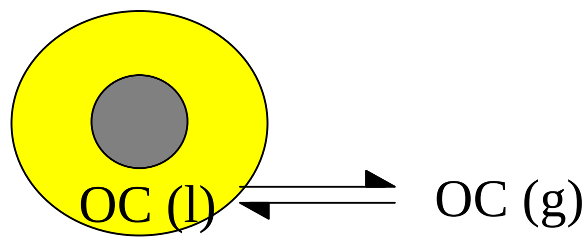
Modules Under Development

- Externally Mixed Aerosols
- Surrogate Species

Type A (Aqueous)



Type B (Organic)



e.g., Malic acid,
Glyoxalic acid

e.g., Octadecanoic acid

Data Needs

Chemistry

- Products studies
- Mechanisms
- SOA composition

Emissions

- Individual terpene species
- Sesquiterpenes and oxygenates
- Need instrument development work

SOA Partition

- Identity of SOA species
- Theoretical development

Acknowledgement

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